Cluster Compounds

A Trihydroxy Tin Group That Resists Oligomerization in the Trinuclear Nickel Cluster $[Ni_3(\mu\text{-}P,P'\text{-}PPh_2CH_2PPh_2)_3(\mu_3\text{-}L)(\mu_3\text{-}Sn(OH)_3)]$**

*Eugenio Simón-Manso and Clifford P. Kubiak**

The conversion of tin chloride reagents into the corresponding hydroxides typically results in the formation of oligomeric tin oxides.[1–3] We report herein the preparation and reactivity of a trinuclear nickel cluster that is capped by a μ_3-Sn(OH)$_3$ group. This is a rare example of a complex that contains an intact trihydroxy tin group, thus allowing the study of the chemistry of tin hydroxides without interference from competing reactions that form oligomeric tin oxides.

The trichlorostannyl-capped cluster $[Ni_3(\mu\text{-dppm})_3(\mu_3\text{-Cl})(\mu_3\text{-Sn(Cl)}_3]$ (**1**; dppm = bis(diphenylphosphino)methane) is a dark-green diamagnetic species, the $^{31}P\{^{1}H\}$ NMR spectrum of which displays a singlet at $\delta = -2.3$ ppm that is flanked by satellites arising from coupling to the trichlorostannyl group ($^{2}J_{(^{31}P-^{119}Sn,^{117}Sn)} = 138$ Hz (unresolved)). The properties of cluster **1** are similar to the closely related μ-iodo-capped cluster that was reported recently.[4] The molecular structure of the trichlorostannyl-capped cluster **1** is presented in Figure 1. The three chlorine atoms of the μ_3-SnCl$_3$ are staggered with respect to the three nickel atoms, resulting in an approximately octahedral coordination environment at the tin atom and approximate C_{3v} symmetry for the cluster.

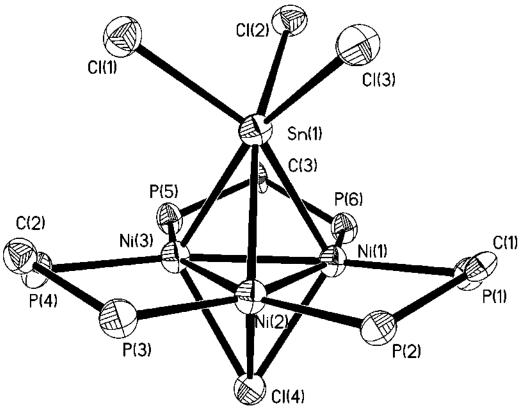
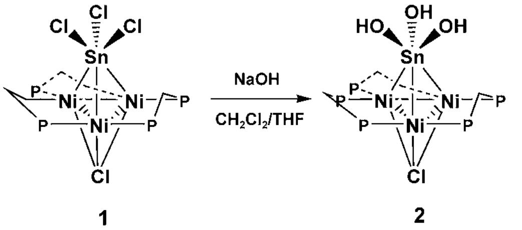


Figure 1. ORTEP diagram of complex **1** (thermal ellipsoids set at 50 % probability). Selected bond lengths [Å] and angles [°]: Sn(1)-Cl(3) 2.457(3), Sn(1)-Cl(2) 2.466(3), Sn(1)-Cl(1) 2.473(3), Sn(1)-Ni(2) 2.5960(16), Sn(1)-Ni(3) 2.6185(16), Ni(1)-Ni(2) 2.4593(18), Ni(1)-Ni(3) 2.4829(18), Ni(2)-Ni(3) 2.4825(16), Ni-P(average) 2.2180(18); Cl(3)-Sn(1)-Cl(2) 88.36(9), Ni(2)-Ni(1)-Ni(3) 60.30(5), P(1)-Ni(1)-Sn(1) 107.20(10), P(6)-Ni(1)-Sn(1), 108.91(10).

Cluster **1** may be converted into the trihydroxystannyl-capped cluster $[Ni_3(\mu\text{-dppm})_3(\mu_3\text{-Cl})(\mu_3\text{-Sn(OH)}_3]$ (**2**) in high yield by treatment with in situ hydrolyzed NaH in a CH_2Cl_2/THF solvent mixture [Eq. (1)]. Use of NaH provides higher yields than direct use of NaOH, most likely because the NaH powder gives more highly dispersed NaOH than the poorly soluble NaOH pellets.



(1)

Cluster **2** is a deep-blue diamagnetic solid whose $^{31}P\{^{1}H\}$ NMR spectrum displays a singlet with satellites at $\delta = -0.1$ ppm ($^{2}J_{(^{31}P-^{119}Sn,^{117}Sn)} = 122$ Hz (unresolved)). The unit cell of crystals of **2** has three independent molecules per unit cell and was solved in space group *P*3. The molecular structure of **2** is presented in Figure 2. The structure reveals a μ_3-Sn(OH)$_3$ group capping a triangular Ni$_3$ cluster in a staggered conformation. Overall, the bond parameters of **2** are quite similar to the μ_3-SnCl$_3$-capped precursor **1** and the cluster $[Ni_3(\mu\text{-dppm})_3(\mu_3\text{-I})(\mu_3\text{-SnCl}_3]$.[4] However, the solid-state crystal structure of **2** reveals that the clusters are organized in pairs with the two Sn(OH)$_3$ groups facing each other in a crystallographically imposed threefold staggered conformation (Figure 3).

The face-to-face arrangement of pairs of Sn(OH)$_3$ groups suggests partial intermolecular hydrogen bonding in the solid state. The intermolecular distances between pairs of O atoms of the hydroxy groups (Figure 3 A) fall in the narrow range of 2.983(10)–3.003(10) Å. This is at the long end of the range

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[*] Dr. E. Simón-Manso, Prof. C. P. Kubiak
Department of Chemistry & Biochemistry
University of California-San Diego
La Jolla, CA 92093-0358 (USA)
Fax: (+1) 858-534-5383
E-mail: ckubiak@ucsd.edu

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Supporting information for this article (ORTEP diagram for complex **6**, spectroscopic data, and MS data) is available on the WWW under http://www.angewandte.org or from the author.

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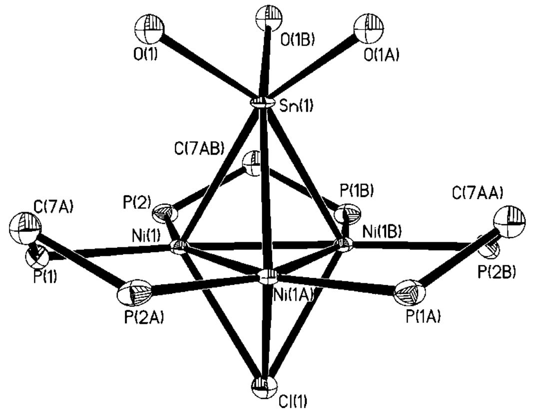


Figure 2. ORTEP diagram of complex **2** (thermal ellipsoids set at 50 % probability). Selected bond lengths [Å] and angles [°]: Sn(1)-O(1) 2.039(7), Sn(1)-Ni(1) 2.6355(17), Ni-P(average) 2.193(3), Ni(1)-Cl(1) 2.429(4), Ni(1)-Ni(1A) 2.451(2); O(1)-Sn(1)-O(1A) 94.0(3), O(1)-Sn(1)-Ni(1) 105.4(2), Ni(1)-Sn(1)-Ni(1A) 55.41(5), Ni(1)-Ni(1A)-Ni(1B) 60.0.

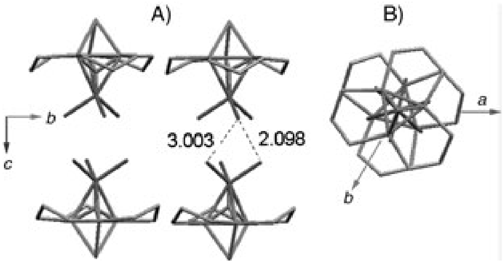


Figure 3. Packing diagram for the crystal structure of complex **2** showing the pairing-up of the clusters: A) side view, B) top view.

normally associated with relatively weak O–H···O hydrogen bonding.[5] The fact that the μ_3-Sn(OH)$_3$ group of the cluster **2** resists oligomerization is likely to be the result of the considerable steric influences of the {Ni$_3$(dppm)$_3$} framework. A space-filling diagram of the structure of **2** shows that the μ_3-Sn(OH)$_3$ group sits in a hydrophobic pocket created by the phenyl rings of the three dppm ligands (Figure 4).

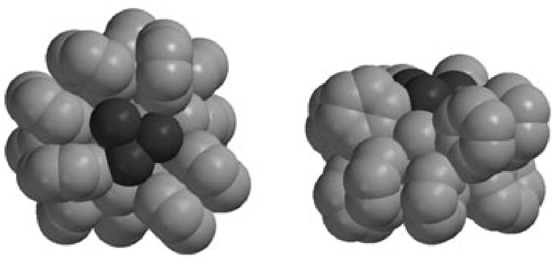
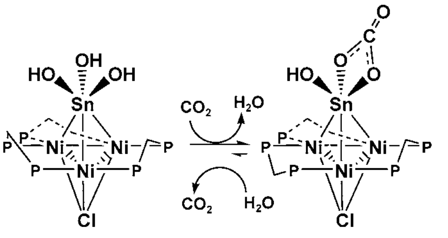


Figure 4. Two projections of the space-filling diagram of the structure of complex **2**; the three oxygen atoms of the μ_3-Sn(OH)$_3$ groups are shown in darker gray.

The μ_3-Sn(OH)$_3$ group of cluster **2** exhibits nucleophilic addition to carbon dioxide and epoxides. Bubbling CO$_2$ through solutions of complex **2** in CH$_2$Cl$_2$ or THF results in an immediate color change from deep-blue to purple and the quantitative formation of the η^2-carbonate complex **3** [Eq. (2)].



2 **3** (2)

Characteristic bands for carbonate, $\tilde{\nu}_{CO} = 1634$ and 1669 cm^{-1}, are observed in the solid-state and solution IR spectra of cluster **3**. The ^{31}P{^{1}H} NMR spectrum is a singlet flanked by two satellites at $\delta = +1.1$ ppm ($^2J_{(^{31}P-^{119}Sn,^{117}Sn)} =$ 128 Hz (unresolved)). Formation of the carbonate cluster is accompanied by H$_2$O elimination, and the reaction between the μ_3-Sn(OH)$_3$ cluster **2** and the μ_3-Sn(OH)(η^2-CO$_3$) cluster **3** is completely reversible [Eq. (2)]. The molecular structure of cluster **3** is presented in Figure 5.

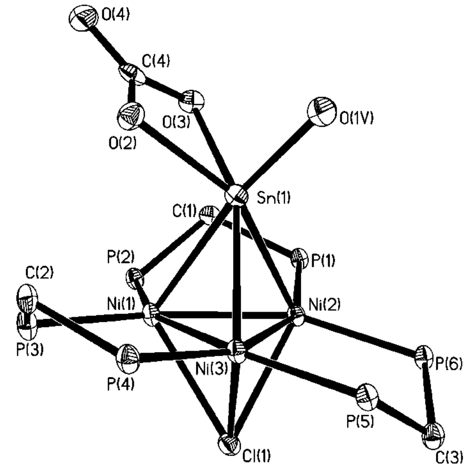
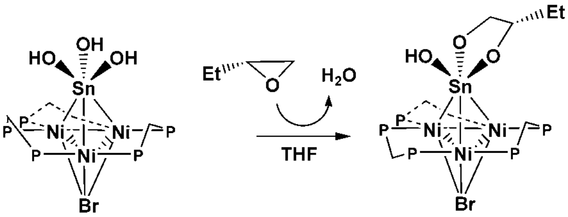


Figure 5. ORTEP diagram for complex **3** (thermal ellipsoids set at 50 % probability). Selected bond lengths [Å] and angles [°]: Sn(1)-O(3) 2.121(3), Sn(1)-Ni(3) 2.5197(7), Ni(1)-Ni(3) 2.4344(8), Ni(1)-Cl(1) 2.4705(14), Ni(3)-Cl(1) 2.3543(13), O(4)-C(4) 1.223(6), O(2)-C(4) 1.325(6); O(1V)-Sn(1)-O(3) 90.39(9), O(3)-Sn(1)-O(2) 61.80(13), Ni(3)-Sn(1)-Ni(2) 57.42(2), Ni(2)-Ni(1)-Ni(3) 61.01(3), O(3)-C(4)-O(2) 111.8(4).

The carbonate-capped cluster **3** exhibits one of the most distorted angles yet observed in a carbonate complex, ∢O(3)-Sn(1)-O(2) = 61.80(13)°, and a highly distorted octahedral coordination geometry around the tin atom.[6] The carbonate group is also highly distorted from ideal D_{3h} symmetry (ideal: all C–O ≈ 1.28–1.29 Å) with longer C–O bond lengths for the oxygen atoms coordinated to tin (average: 1.330(3) Å), and a shorter C–O bond lengths for the uncoordinated oxygen atom (1.223(6) Å). The O(3)-C(4)-O(2) bond angle is narrow (111.8°), reflecting a strained four-membered ring.

Cluster **2** also undergoes ring-opening addition of 1,2-epoxybutane to give the 1,2-diolate tin cluster [Ni_3(μ-$PPh_2CH_2PPh_2$)$_3$($μ_3$-Cl)($μ_3$-Sn(OH)($η^2$-O-$CH_2CH(C_2H_5)$-O)] (**4**). Cluster **4** was characterized by mass spectrometry and NMR spectroscopy (see Supporting Information). This reaction results in isomeric mixtures, and we were unable to isolate a suitable crystal of **4** for X-ray characterization. However, the closely related $μ_3$-Br derivative [Ni_3(μ-$PPh_2CH_2PPh_2$)$_3$($μ_3$-Br)($μ_3$-Sn(OH)$_3$)] (**5**; prepared from [Ni_3{μ-P,P′-dppm}$_3$($μ_3$-Br)($μ_3$-$SnBr_3$)] (**6**), see Experimental Section) reacts with 1,2-epoxybutane to afford the 1,2-diolate cluster [Ni_3(μ-$PPh_2CH_2PPh_2$)$_3$($μ_3$-Br){$μ_3$-Sn(OH)[$η^2$-OCH_2-$CH(C_2H_5)O$]}] (**7**) as a crystalline material [Eq. (3)].



(3)

5 **7**

Cluster **7** is a turquoise-blue diamagnetic solid, and its $^{31}P\{^1H\}$ NMR spectrum displays a singlet with satellites at $\delta = -1.9$ ppm ($^2J_{(^{31}P-^{119}Sn,^{117}Sn)} = 98$ Hz (unresolved)). The molecular structure of complex **7** shows a $OCH_2CH(C_2H_5)O$ diolate group coordinated to the tin atom in a chelated $η^2$ fashion (Figure 6). The large thermal parameter for the C(5) atom in the direction perpendicular to the O(1)-O(2)-C(5)-C(4) plane is the result of superposition of two different orientations of the molecule in the crystal lattice. The centrosymmetric *P*2(1)/*c* space group confirms the presence of a 50:50 *R*/*S* racemic mixture in the crystal.

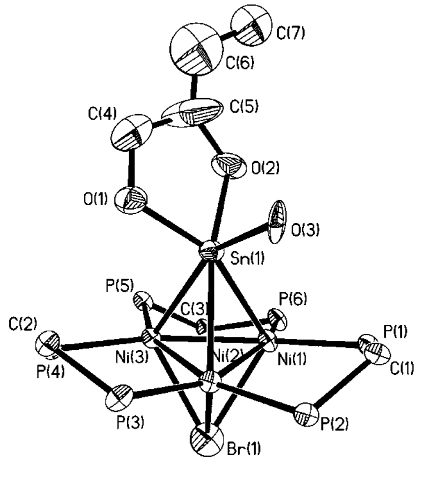


Figure 6. ORTEP diagram for complex **7** (thermal ellipsoids set as 50 % probability). Selected bond lengths [Å] and angles [°]. Ni(1)-Ni(3) 2.4307(14), Ni(1)-Br(1) 2.4470(16), Ni(1)-Sn(1) 2.6238(12), Ni(2)-Sn(1) 2.6173(12), Ni(3)-Sn(1) 2.5873(11), Sn(1)-O(2) 2.020(7), Sn(1)-O(1) 2.043(7), Sn(1)-O(3) 2.178(7); Ni(3)-Ni(1)-Ni(2) 59.60(4), Ni(3)-Ni(1)-Sn(1) 61.44(4), Ni(3)-Ni(2)-Ni(1) 60.17(4).

Complexes **2** and **5** constitute rare examples of tin trihydroxy compounds. A search of more than 250 000 structures in the Cambridge Crystallographic Data Center[7–9] does not yield any structurally characterized compounds that have an intact $Sn(OH)_3$ fragment. The search recalls only one example of a Sn($η^2$-CO_3) group. Of course, the usual tendency for such groups is to dimerize or even polymerize.[1–3]

In conclusion, we report a straightforward synthetic pathway that leads to a new series of trihydroxy tin trinuclear nickel clusters. The reactivity of these clusters is centered at the octahedrally coordinated tin atom. The $Sn(OH)_3$ groups of clusters **2** and **5** resist oligomerization and display high nucleophilicity leading to reversible formation of an $η^2$-carbonato-tin-capped cluster in the presence of CO_2 and ring opening of 1,2-epoxybutane to the corresponding tin-coordinated diolate.

Experimental Section

1: A solution of $SnCl_2$ (274 mg, 1.46 mmol) dissolved in THF was added to a mixture of [$Ni(cod)_2$] (400 mg, 1.46 mmol; cod = cyclooctadiene), dppm (845 mg, 2.2 mmol), and [$Ni(acac)_2$] (186 mg, 0.73 mmol; acac = 2,4-pentanedione) in THF (20 mL). The solution turned dark-green immediately and a green precipitate appeared. The solid was collected by filtration and washed with diethyl ether. Recrystallization from CH_2Cl_2/diethyl ether gave pure **1** (690 mg, 59 %). Elemental analysis (%) calcd for $C_{75}H_{66}Cl_4Ni_3P_6Sn$: C 56.66, H 4.18; found: C 56.29, H 4.88; $^{31}P\{^1H\}$ NMR (121 MHz, [D_8]THF, 295 K): $\delta = -2.3$ ppm (s, sat. $^2J_{(^{31}P-^{119}Sn,^{117}Sn)} = 138$ Hz (unresolved)).

2: Solid NaH (10 mg, 0.416 mmol) was suspended in a solution of **1** (200 mg, 0.125 mmol) dissolved in a mixture of CH_2Cl_2/THF (3:2). Water (8 μL, 0.444 mmol) was injected through a septum into this suspension and H_2 evolved. After 2 h the reaction was complete (followed by ^{31}P NMR spectroscopy). The solvent was evaporated to dryness, and the residue was kept under vacuum overnight. Extraction with CH_2Cl_2 and evaporation of the solvent gave a deep-blue solid (150 mg, 73 %). Elemental analysis (%) calcd for $C_{77}H_{71}Cl_3Ni_3O_3P_6Sn$ (**2**·CH_2Cl_2): C 56.69, H 4.39; found: C 56.47, H, 4.62. $^{31}P\{^1H\}$ NMR (121 MHz, [D_8]THF, 295 K): $\delta = -0.1$ ppm (s, sat. $^2J_{(^{31}P-^{119}Sn,^{117}Sn)} = 122$ Hz (unresolved)). IR (KBr): $\tilde{\nu}_{OH} = 3658$ cm^{-1} (br).

3: Carbon dioxide was bubbled through a solution of **2** (100 mg, 0.06 mmol) dissolved in CH_2Cl_2 (5 mL). The color of the solution changed from deep-blue to deep-purple immediately. Complete conversion was verified by ^{31}P NMR spectroscopy. Elemental analysis (%) calcd for $C_{77}H_{69}Cl_3Ni_3O_4P_6Sn$ (**3**·CH_2Cl_2): C 56.23, H 4.19; found: C 56.40, H 4.67; $^{31}P\{^1H\}$ NMR (121 MHz, [D_8]THF, 295 K): $\delta = 1.1$ ppm (s, sat. $^2J_{(^{31}P-^{119}Sn,^{117}Sn)} = 128$ Hz (unresolved). IR (KBr): $\tilde{\nu} = 1634, 1669$ cm^{-1}.

5: Using cluster **6** as starting material (see below) and the same synthetic procedure described for cluster **2**, compound **5** was obtained as a deep-blue solid (110 mg, 64 %). Elemental analysis (%) calcd for $C_{75}H_{69}BrNi_3O_3P_6Sn$: C 57.05, H 4.40; found: C 58.34, H 4.95. $^{31}P\{^1H\}$ NMR (121 MHz, [D_8]THF, 295 K): $\delta = -1.1$ ppm (s, sat. $^2J_{(^{31}P-^{119}Sn,^{117}Sn)} = 115$ Hz (unresolved)); IR (KBr): $\tilde{\nu}_{OH} = 3668$ cm^{-1} (br).

[Ni_3{μ-P,P′-dppm}$_3$($μ_3$-Br)($μ_3$-$SnBr_3$)] (**6**): Solid $SnBr_2$ (≈5 mg) was added to a suspension of KBr (42 mg, 0.36 mmol) in a solution of **1** (200 mg, 0.125 mmol) dissolved in THF (10 mL). After two days the reaction was complete (verified by ^{31}P NMR spectroscopy) and the color of the solution had changed from dark-green to brown–green. The volume was reduced by evaporation under vacuum to 5 mL, and diethyl ether (5 mL) was added. The solid was collected by filtration and washed with diethyl ether (175 mg, 75 %). Elemental analysis (%) calcd for $C_{79}H_{74}Br_4Ni_3OP_6Sn$ (**6**·THF): C 51.57, H 4.02; found: C

52.11, H 4.13. $^{31}P\{^1H\}$ NMR (121 MHz, $[D_8]$THF, 295 K): $\delta = -2.1$ (s, sat. ${}^2J_{(^{31}P-^{119}Sn,^{117}Sn)} = 140$ Hz (unresolved)).

7: 1,2-Epoxybutane (30 mg, 0.22 mmol) was added to a solution of cluster **5** (250 mg, 0.16 mmol) in THF (10 mL). The solution was gently heated and an immediate color change from deep-blue to turquoise was observed. The ^{31}P NMR spectrum shows no signal for the starting cluster **5** and only one singlet at $\delta = -1.9$ ppm (185 mg, 63 %). MALDI-MS $[Ni_3(dppm)_3Br\{Sn(OH)[OCH_2CH(C_2H_5)O]\}H]^+$ 1633 *m*/*z*; $^{31}P\{^1H\}$ NMR (121 MHz, $[D_8]$THF, 295 K): $\delta = -1.9$ ppm (s, sat. ${}^2J_{(^{31}P-^{119}Sn,^{117}Sn)} = 98$ Hz (unresolved)).

CCDC-250075–CCDC-250079 (**1**, **2**, **3**, **6**, and **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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